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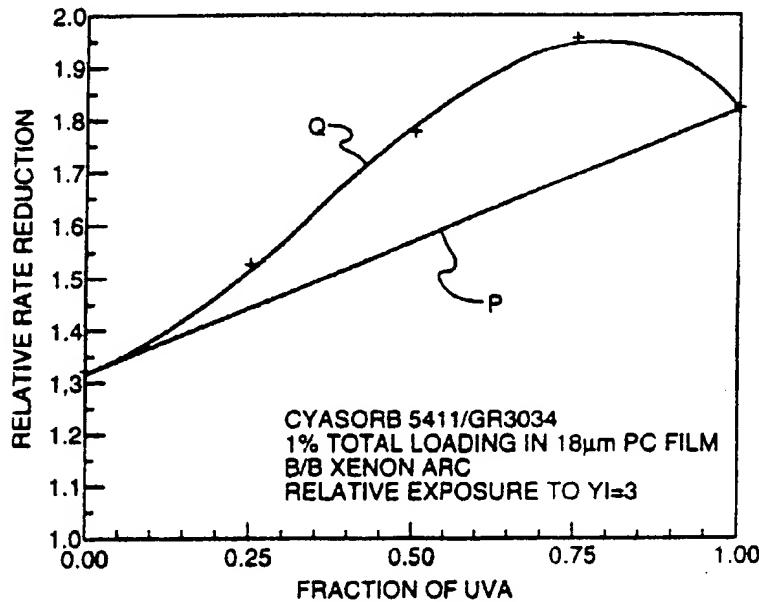
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(54) Polycarbonate compositions comprising hindered amine light stabilizers and ultraviolet light absorbers

(57) Weatherable polycarbonate compositions (formulations or blends) comprise at least one of a piperazinone and piperazine dione based HALS, and at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA. The combination of

these HALS and UVA exhibits a synergy that results in enhanced protection of the polycarbonate compositions by imparting photostability to the polycarbonate formulations, thereby reducing yellowing or other forms of light induced degradation.



EP 0 900 823 A2

**Description****FIELD OF INVENTION**

5 [0001] The instant invention relates to weatherable compositions (blends and formulations) comprising polycarbonate, hindered amines light stabilizers, and ultraviolet light absorbers.

**BACKGROUND OF THE INVENTION**

10 [0002] Formulations and blends comprising polycarbonates are known to degrade upon prolonged exposure to sun-light or other forms of light. One of the effects observed is yellowing of the polycarbonate blend/formulation. This problem has been alleviated by the use of light absorbers or light blockers in the polycarbonate blends. Thus ultraviolet light absorbers (UVA) are known to be used in polycarbonate formulations to protect these formulations from degradation due to exposure to different forms of light.

15 [0003] Use of Hindered Amine Light Stabilizers (HALS) to stabilize polyolefins has been known. Commercially used HALS have been based mainly on 2,2,6,6-tetramethyl piperidine, except for those based on piperazinones. U.S. Patent Numbers 4,190,571; 4,292,240; 4,480,092; and 5,071,981 disclose some of the piperazinone based HALS. In addition while United States Patent Numbers 3,919,234, 3,920,659 and 4,208,522 disclose some piperazine dione based HALS.

20 [0004] The use of HALS in polycarbonates is not very common. The stabilizing effect of HALS on polycarbonate formulations/blends has been described as "minor", see for example Thompson and Klemchuk, in Polymer Durability; R. L. Clough et al., ACS Advances in Chemistry 249, 1995, pp 303-317. The use of UVA in polycarbonate formulations has provided a way to retard the rate of degradation of polycarbonates as a result of exposure to light. This method however does not offer a complete protection of polycarbonate formulations from light induced degradation or discoloration. There is thus a continued need for a method or formulation that will help protect polycarbonate based formulations/blends from degradation or discoloration due to exposure to light.

25 [0005] It has been surprisingly found that use of the piperazinone and piperazine dione based HALS, and the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA in polycarbonate compositions, exhibits a synergistic effect in protecting the polycarbonate compositions from light induced degradation. This synergistic effect increases the photostability of polycarbonate compositions thereby slowing the yellowing and degradation of polycarbonate compositions.

**SUMMARY OF THE INVENTION**

30 [0006] The instant invention provides a composition comprising a polycarbonate, at least one of a piperazinone and a piperazine dione based HALS, and at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA. Incorporation of the piperazinone and piperazine dione based HALS, and the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA in the polycarbonate composition surprisingly displays a synergistic effect in protecting the polycarbonates from the undesired degradation or discoloration due to exposure to light, thereby rendering weatherable polycarbonate compositions.

**BRIEF DESCRIPTION OF DRAWINGS**

40 [0007] The Figure plots exposures required to attain a YI of 3.0 (relative to an unstabilized control, Sample 1) for BPA polycarbonate films containing various ratios of UVA to HALS at 1% by weight of the total polycarbonate composition.

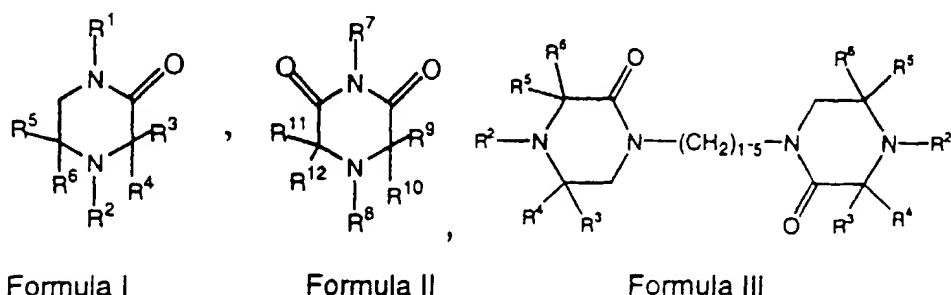
**DETAILED DESCRIPTION OF THE INVENTION**

45 [0008] The present invention provides a composition comprising, a polycarbonate, at least one of a piperazinone and piperazine dione based HALS, and at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA. Another embodiment of the invention provides a composition wherein, (a) the polycarbonate comprises from about 90% to about 99.9% by weight of the total composition; and (b) the piperazinone and piperazine dione based HALS and the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA, taken together, comprise from about 0.1% to about 10% by weight of the total composition, the ratio of the piperazinone and piperazine dione based HALS to the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA being from about 5:95 to about 90:10. In a further preferred embodiment is provided a composition wherein the ratio of the piperazinone and piperazine dione based HALS to that of the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA is from about 5:95 to about 20:80. Another preferred embodiment provides a composition

wherein the ratio of the piperazinone and piperazine dione based HALS to that of the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA is from about 20:80 to about 75:25.

[0009] A second aspect of the instant invention provides a composition comprising, (a) a polycarbonate; (b) at least one of a piperazinone and piperazine dione based HALS; (c) at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA; (d) an additive; and (e) a blend stock. In one of its embodiment is provided a composition wherein: (a) the polycarbonate comprises from about 10% to about 99.9% by weight of the total composition; (b) the piperazinone or piperazine dione based HALS and the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA, taken together, comprise from about 0.05% to about 10% by weight of the total composition; (c) additives comprise from about 0.01% to about 25% by weight of the total composition; and (d) the blend stock comprises from about 0% to about 89% by weight of the total composition. The preferred polycarbonate is BPA polycarbonate.

[0010] Another preferred embodiment provides a composition wherein the piperazinone or piperazine dione based HALS is selected from:

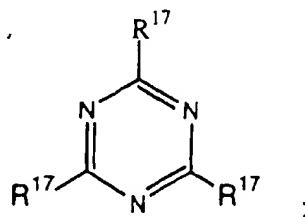


25 Formula I

20 Formula II

Formula III

and



30 Formula IV

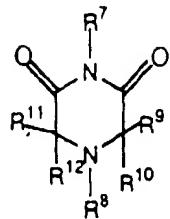
wherein:

45 R<sup>1</sup> and R<sup>2</sup> are independently C<sub>1-24</sub> alkyl, hydrogen, acyl, benzyl, C<sub>1-12</sub> haloalkyl, C<sub>2-14</sub> alkenyl, unsubstituted C<sub>7-14</sub> aralkyl, or carboalkoxy; R<sup>2</sup> optionally also represents oxygen; R<sup>3</sup> and R<sup>4</sup> independently represent C<sub>1-18</sub> haloalkyl, C<sub>1-18</sub> alkyl, C<sub>5-18</sub> cycloalkyl, C<sub>2-18</sub> alkenyl, or unsubstituted C<sub>7-18</sub> aralkyl; or R<sup>3</sup> and R<sup>4</sup>, when taken together with the carbon to which they are attached, form a C<sub>4-12</sub> alicyclic ring; R<sup>5</sup> and R<sup>6</sup> are independently C<sub>1-18</sub> haloalkyl, C<sub>1-18</sub> alkyl, C<sub>2-18</sub> alkenyl, or unsubstituted C<sub>7-18</sub> aralkyl; or R<sup>5</sup> and R<sup>6</sup> when taken together with the carbon atom to which they are attached, form a C<sub>4-12</sub> alicyclic ring; R<sup>7</sup> is C<sub>1-20</sub> alkyl, benzyl,



55 or





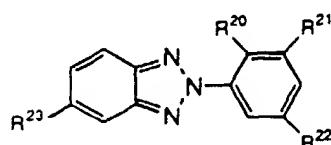
10 Formula II

wherein:

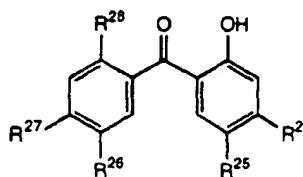
R<sup>9</sup> and R<sup>10</sup> independently represent methyl; or R<sup>9</sup> and R<sup>10</sup>, when taken together with the carbon to which they are attached, form a cyclohexyl ring; and

R<sup>11</sup> and R<sup>12</sup> independently methyl; or R<sup>11</sup> and R<sup>12</sup>, when taken together with the carbon atom to which they are attached, form a cyclohexyl ring.

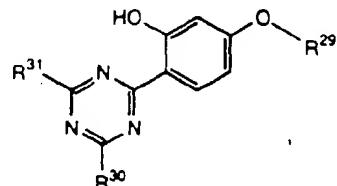
[0012] The ultraviolet light absorbers (UVA) useful in the present invention are those which are generally compatible with polycarbonates in general. Preferred are benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA represented by the following structural formulae:



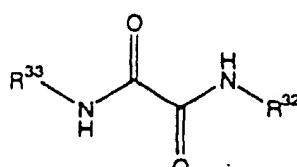
30 Formula V



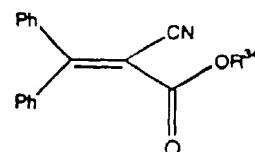
Formula VI



Formula VII



40 Formula VIII



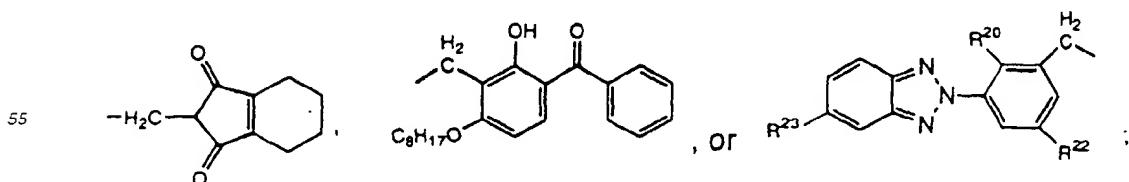
45 Formula IX

wherein:

R<sup>20</sup> is OH;

R<sup>21</sup> is C<sub>1</sub>-C<sub>15</sub> branched or straight chain alkyl, C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>,

50



R<sup>22</sup> is C<sub>1</sub>-C<sub>15</sub> branched or straight chain alkyl, -C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, -(CH<sub>2</sub>)<sub>2</sub>-C(O)-O- C<sub>8</sub>H<sub>17</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-C(O)-O-(C<sub>2</sub>H<sub>4</sub>O)<sub>8</sub>-H, -CH<sub>2</sub>CH<sub>2</sub>O--C(O)-C(CH<sub>3</sub>)=CH<sub>2</sub>, or-C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-CH<sub>3</sub>;

R<sup>23</sup> is H or Cl;

R<sup>24</sup> is OH, -OC<sub>1</sub>-C<sub>12</sub>alkyl, -O-CH<sub>2</sub>CH=CH<sub>2</sub>, -O-(CH<sub>2</sub>)<sub>3</sub>Si(OEt)<sub>3</sub>, -OCH<sub>2</sub>COOH, -O(CH<sub>2</sub>)<sub>2</sub>OC(O)-CH=CH<sub>2</sub>, -OCH<sub>2</sub>CH<sub>2</sub>OH, or -O-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>O-C<sub>8</sub>H<sub>17</sub>;

R<sup>25</sup> is H, benzoyl, SO<sub>3</sub>H, or SO<sub>3</sub>Na;

R<sup>26</sup> is H, SO<sub>3</sub>H, or SO<sub>3</sub>Na;

R<sup>27</sup> is H, OH, OCH<sub>3</sub>, or -C(CH<sub>3</sub>)<sub>3</sub>;

R<sup>28</sup> is H or OH;

R<sup>29</sup> is -C<sub>1</sub>-C<sub>10</sub> alkyl, or -C<sub>1</sub>-<sub>6</sub> branched or straight chain alkyl-O-C<sub>10</sub>-C<sub>15</sub> straight chain alkyl;

R<sup>30</sup> and R<sup>31</sup> independently represent a phenyl radical optionally substituted with up to two C<sub>1</sub>-C<sub>4</sub> alkyl substituents;

R<sup>32</sup> and R<sup>33</sup> independently represent aryl groups substituted with at least one of C<sub>1</sub>-C<sub>12</sub> alkyl or C<sub>1</sub>-C<sub>8</sub> alkoxy group; and

R<sup>34</sup> represents C<sub>1</sub>-C<sub>8</sub> straight chain alkyl group, C<sub>4</sub>-C<sub>8</sub> branched alkyl group, or a C<sub>1</sub>-C<sub>6</sub> hydroxy alkyl group.

[0013] Further preferred UVA's are those represented by Formula V, Formula VI, and Formula VII wherein:

R<sup>20</sup> is OH;

R<sup>21</sup> is C(CH<sub>3</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, C(CH<sub>3</sub>)<sub>2</sub>Ph, or CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>;

R<sup>22</sup> is CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>Ph, CH<sub>2</sub>-CH<sub>2</sub>-C(O)-O-(C<sub>2</sub>H<sub>4</sub>OH)<sub>8</sub>, or C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>3</sub>;

R<sup>23</sup> is H;

R<sup>24</sup> is OH or OC<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>25</sup> is H or benzoyl;

R<sup>26</sup> is H;

R<sup>27</sup> is H, OH, or OCH<sub>3</sub>;

R<sup>28</sup> is H or OH;

R<sup>29</sup> is C<sub>1</sub>-<sub>4</sub> alkyl; and

R<sup>30</sup> and R<sup>31</sup> independently represent a phenyl radical substituted with C<sub>1</sub>-<sub>2</sub> alkyl. Specifically preferred UVA are 2-(2'-hydroxyaryl benzotriazole), 2,4-diaryl-6-(2'-hydroxyaryl)-s-triazines, and 4,6-dibenzoyl resorcinol.

[0014] As used in the instant invention a polycarbonate comprises multiple structural units represented by the formula



wherein A<sup>1</sup> is a divalent aromatic hydrocarbon radical. Suitable A<sup>1</sup> radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)phenylene, 2,2-bis(4-phenylene)propane and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438.

[0015] The A<sup>1</sup> radical preferably has the formula



wherein each of A<sup>2</sup> and A<sup>3</sup> is a mono cyclic divalent aromatic hydrocarbon radical and Y is a bridging hydrocarbon radical in which one or two atoms separate A<sup>2</sup> from A<sup>3</sup>. The free valence bonds in formula X are usually in the meta or para positions of A<sup>2</sup> and A<sup>3</sup> in relation to Y. Compounds in which A<sup>1</sup> has formula XI are bisphenols, and for the sake of brevity the term "bisphenol" is sometimes used herein to designate the dihydroxy-substituted aromatic hydrocarbons; it should be understood, however, that non-bisphenol compounds of this type may also be employed as appropriate.

[0016] In formula XI, the A<sup>2</sup> and A<sup>3</sup> values may be unsubstituted phenylene or hydrocarbon-substituted derivatives thereof, illustrative substituents (one or more) being alkyl and alkenyl. Unsubstituted phenylene radicals are preferred. Both A<sup>2</sup> and A<sup>3</sup> are preferably p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

[0017] The bridging radical, Y, is one in which one or two atoms, preferably one, separate A<sup>2</sup> from A<sup>3</sup>. Illustrative radicals of this type are methylene, cyclohexylmethylene, 2-[2.2.1]-bicycloheptylmethylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene and adamantylidene; gem-alkylene (alkylidene) radicals are preferred. Also included, however, are unsaturated radicals. For reasons of availability and

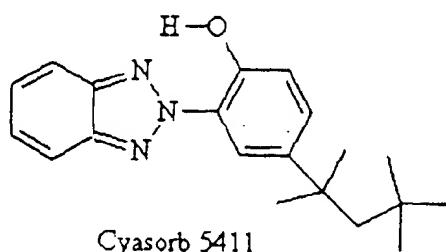
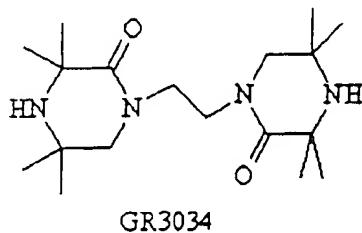
particular suitability for the purposes of this invention, the preferred bisphenol is 2,2-bis(4-hydroxyphenyl)propane ("BPA"), in which Y is isopropylidene and A<sup>2</sup> and A<sup>3</sup> are each p-phenylene. A detailed description of polycarbonates used in the instant invention is described in U.S. Patent Nos. 4,125,572; 3,028,365; 3,334,154; and 3,915,926; all of which are incorporated herein by reference.

5 [0018] The compositions of the instant invention comprise at least one of a piperazinone and piperazine dione based HALS, and at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA. It should be noted that one or a mixture of more than one piperazinone and piperazine dione based HALS along with one or a mixture of more than one benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA can be used as part of the instantly claimed compositions. The piperazinone and piperazine dione based HALS are generally represented by Formula I, Formula II, Formula III, or Formula IV while the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA are represented by Formula V, Formula VI, Formula VII, Formula VIII, and Formula IX. Also as used herein, additives may include such materials as colorants, whitening agents, thermal stabilizers, metal deactivators, impact modifiers, extenders, antistatic agents, and processing aids. The different additives that can be incorporated in the compositions of the instant invention are commonly used and known to one skilled in the art. Illustrative descriptions of such additives may be found in R. Gachter and H. Muller; Plastics Additives, 4<sup>th</sup> edition, 1993 and are incorporated herein by reference.

10 15 [0019] Also, as used in the instant invention, the phrase blend stock is used to describe one or more ingredients represented by aromatic polyesters, aliphatic polyesters, and styrenic polymers. Examples of blend stocks include poly (2,4-butylene terephthalate, poly(ethylene terephthalate), acrylonitrile-butadienestyrene copolymer (ABS), styrene-acrylonitrile copolymer (SAN, styreneacrylonitrile-acrylate copolymers (ASA), and poly(1,4-cyclohexanedimethanol-1,4-cyclohexanedicarboxylate) (PCCD).

#### EXPERIMENTAL DETAILS

25 [0020] Mixtures of UVA and HALS impart a synergistic effect when used in combination. Thus, rather than using a particular amount of UVA or HALS alone in a formulation, it is advantageous to use a mixture of UVA and HALS. This effect will generally be independent of the structure of the UVA and independent of the structure of the HALS, as long as the HALS is compatible with the polycarbonate and the UVA has significant absorption in the range of 295-330 nm. A typical UVA used is Cyasorb® 5411, which is a product of Cytec Corporation and belongs to the benzotriazole class 30 of UVA. The piperazinone class of HALS, typified by Goodrite® 3034 (GR3034), is an illustrative example of an effective class of HALS.



45 [0021] The ratio of UVA to HALS, at which the maximum synergism occurs, is probably dependent on the thickness of the sample, the nature of the colorants that might be present, the absorptivity of the UVA, and the light exposure conditions. The following data shows maximum effectiveness at a ratio of approximately 0.75 UVA to 0.25 HALS in approximately 18 microns thick polycarbonate film.

50 Example 1 : Photostability of solvent-cast films.

[0022] BPA polycarbonate (BPA-PC) films approximately 18 microns thick were cast from methylene chloride by drawing 20% solids solutions on a glass plate using a 6 mil doctor blade. The HALS and UVA, taken together, were added to the methylene chloride solution at a total of 1% by weight of the polycarbonate composition in the ratios shown in Table 1. The UVA was Cyasob® 5411 (a benzotriazole based UVA) and the HALS was Goodrite® 3034 (a piperazine based HALS).

[0023] Samples were exposed in an Atlas Ci35a xenon arc Weather-ometer equipped with type S borosilicate inner and outer filters. The light cycle was 160 minutes long at an irradiance of 0.77 W/m<sup>2</sup> at 340 nm, black panel temperature

75°C, dry bulb temperature 45°C, and wet bulb depression 10°C. There was a 20 minute dark cycle with water spray during the last 15 minutes. Exposure is measured in total kilojoules (kJ) of irradiance at 340 nm.

[0024] The amount of light exposure for the films to reach a Yellowness Index (YI, ASTM D-1925) of 3.0 are shown in Table 1.

5

Table 1.

Performance of UVA/HALS ratios at 1% of total loading composition				
Sample #	% of UVA	% of HALS	Exposure to YI=3.0	Relative yellowing rate reduction*
10	1	0	870 kJ/m <sup>2</sup>	(1)
	2	0	1580	1.82
	3	0.75	1696	1.95
	4	0.50	1536	1.77
	5	0.25	1391	1.52
	6	1	1145	1.32

\* Calculated by dividing exposure in the previous column by control exposure.

20

[0025] The results are also plotted in the Figure which shows the positive deviation from linearity indicative of a synergistic effect of the combination of UVA and HALS. The straight line (identified by the letter 'P' in the Figure) represents the expected additive/resulting effect, on the photostability of the polycarbonate composition, as a consequence of incorporating the piperazinone based HALS and the benzotriazole based UVA in the BPA-PC. The curve (identified by the letter 'Q' in the Figure) is the actual effect observed, on the photostability of the BPA-PC, as a consequence of incorporating the piperazinone based HALS and the benzotriazole based UVA in the BPA-PC. The positive deviation represented by the curve Q from the expected linearity represented by the line P is indicative of the synergistic effect observed as a result of combining the piperazinone based HALS and the benzotriazole based UVA in the BPA-PC.

25

### Claims

1. A composition comprising:

- (a) a polycarbonate;
- (b) at least one of a piperazinone and piperazine dione based HALS; and
- (c) at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA.

2. A composition of Claim 1 wherein:

- (a) the polycarbonate comprises from about 90% to about 99.9% by weight of the total composition; and
- (b) the piperazinone and piperazine dione based HALS and the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA, taken together comprise from about 0.1% to about 10% by weight of the total composition, the ratio of the piperazinone and piperazine dione based HALS to the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA being from about 5:95 to about 90:10.

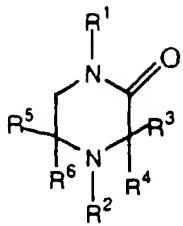
3. A composition of claim 1 or claim 2 wherein the piperazinone and piperazine dione based HALS is selected from:

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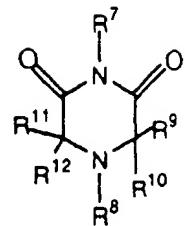
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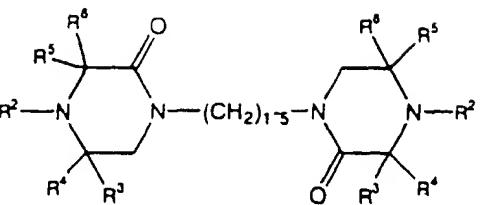
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Formula I

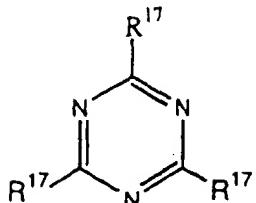


Formula II



Formula III

15 and



Formula IV

30 wherein:

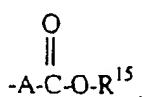
R<sup>1</sup> and R<sup>2</sup> are independently C<sub>1-24</sub> alkyl, hydrogen, acyl, benzyl, C<sub>1-12</sub> haloalkyl, C<sub>1-12</sub> alkyl, C<sub>2-14</sub> alkenyl, unsubstituted C<sub>7-14</sub> aralkyl, or carboalkoxy;

R<sup>2</sup> optionally also represents oxygen;

35 R<sup>3</sup> and R<sup>4</sup> independently represent C<sub>1-18</sub> haloalkyl, C<sub>1-18</sub> alkyl, C<sub>5-18</sub> cycloalkyl, C<sub>2-18</sub> alkenyl, or unsubstituted C<sub>7-18</sub> aralkyl; or R<sup>3</sup> and R<sup>4</sup>, when taken together with the carbon to which they are attached, form a C<sub>5-12</sub> alicyclic ring;

R<sup>5</sup> and R<sup>6</sup> are independently C<sub>1-18</sub> haloalkyl, C<sub>1-18</sub> alkyl, C<sub>2-18</sub> alkenyl, or unsubstituted C<sub>7-18</sub> aralkyl; or R<sup>5</sup> and R<sup>6</sup> when taken together with the carbon atom to which they are attached, form a C<sub>5-12</sub> alicyclic ring;

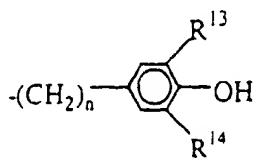
R<sup>7</sup> is C<sub>1-20</sub> alkyl, benzyl,



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or

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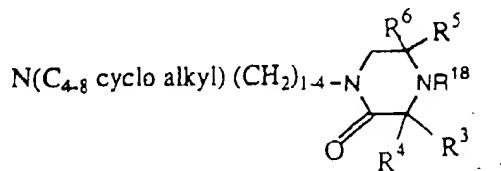
$R^8$  is hydrogen;

R<sup>9</sup> and R<sup>10</sup> independently represent C<sub>1-18</sub> haloalkyl, C<sub>1-18</sub> alkyl, C<sub>5-18</sub> cycloalkyl, C<sub>2-18</sub> is alkenyl, or unsubstituted C<sub>7-18</sub> aralkyl; or R<sup>9</sup> and R<sup>10</sup>, when taken together with the carbon to which they are attached, form a C<sub>5-12</sub> alicyclic ring;

$R^{11}$  and  $R^{12}$  are independently  $C_{1-18}$  haloalkyl,  $C_{1-18}$  alkyl,  $C_{2-18}$  alkenyl, or unsubstituted  $C_{7-18}$  aralkyl; or  $R^{11}$  and  $R^{12}$  when taken together with the carbon atom to which they are attached, form a  $C_{5-12}$  alicyclic ring;  $R^{13}$  and  $R^{14}$  are independently  $C_{1-8}$  alkyl, wherein at least one of said groups is branched on the  $\alpha$  carbon atom;  $R^{15}$  is  $C_{1-20}$  alkyl;

$R^{17}$  is

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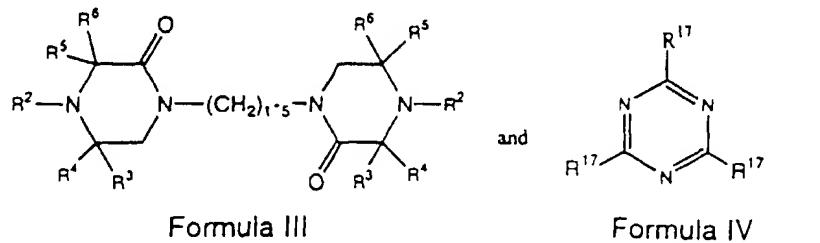


$R^{18}$  is H or C<sub>1-4</sub> alkyl;

A is a straight or branched chain (lower) alkylene having from 1 to 6 carbon atoms optionally substituted with C<sub>1</sub>-C<sub>6</sub> alkyl; and

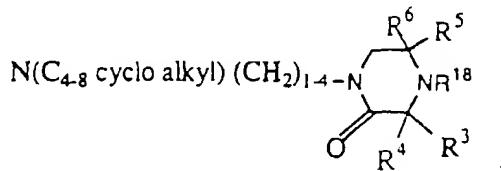
n represents an integer from 1 to 4.

25 4. A composition of Claim 3 wherein the HALS is a piperazinone represented by:



wherein:

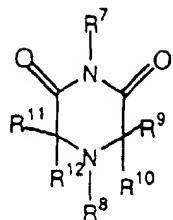
$R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  are each methyl;  
 $R^{17}$  is



and

R<sup>18</sup> is H or C<sub>1-4</sub> alkyl.

5. A composition of claim 3 wherein the HALS is a piperazine dione represented by

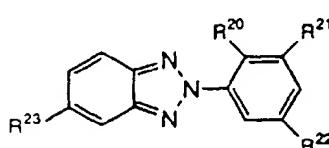


10 Formula II

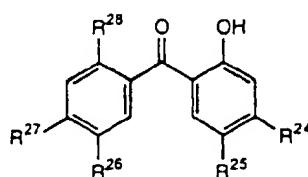
wherein:

15  $R^9$  and  $R^{10}$  independently represent methyl; or  $R^9$  and  $R^{10}$ , when taken together with the carbon to which they are attached, form a cyclohexyl ring; and  
 $R^{11}$  and  $R^{12}$  independently methyl; or  $R^{11}$  and  $R^{12}$ , when taken together with the carbon atom to which they are attached, form a cyclohexyl ring.

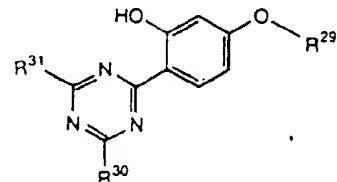
- 20 6. A composition of any preceding claim wherein the benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA is selected from:



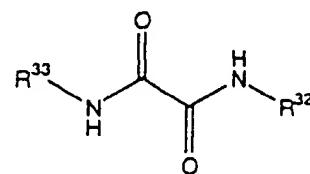
Formula V



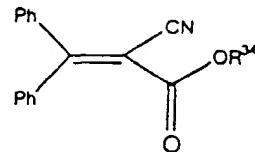
Formula VI



Formula VII



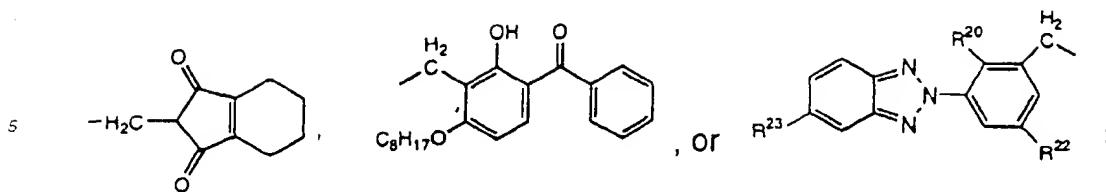
Formula VIII



Formula IX

wherein:

40  $R^{20}$  is OH;  
 $R^{21}$  is C<sub>1</sub>-C<sub>15</sub> branched or straight chain alkyl, C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>,



10 R<sup>22</sup> is C<sub>1</sub>-C<sub>15</sub> branched or straight chain alkyl, -C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, (CH<sub>2</sub>)<sub>2</sub>C(O)-O- C<sub>8</sub>H<sub>17</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-C(O)-O-(C<sub>2</sub>H<sub>4</sub>O)<sub>8</sub>-H, -CH<sub>2</sub>CH<sub>2</sub>O—C(O)-C(CH<sub>3</sub>)=CH<sub>2</sub>, or -C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-CH<sub>3</sub>;

R<sup>23</sup> is H or Cl;

15 R<sup>24</sup> is OH, -OC<sub>1</sub>-C<sub>12</sub>alkyl, -O-CH<sub>2</sub>CH=CH<sub>2</sub>, -O-(CH<sub>2</sub>)<sub>3</sub>Si(OEt)<sub>3</sub>, -OCH<sub>2</sub>COOH, -O(CH<sub>2</sub>)<sub>2</sub>OC(O)-CH=CH<sub>2</sub>, -OCH<sub>2</sub>CH<sub>2</sub>OH, or -O-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>O-C<sub>8</sub>H<sub>17</sub>;

R<sup>25</sup> is H, benzoyl, SO<sub>3</sub>H, or SO<sub>3</sub>Na;;

R<sup>26</sup> is H, SO<sub>3</sub>H, or SO<sub>3</sub>Na;

R<sup>27</sup> is H, OH, OCH<sub>3</sub>, or -C(CH<sub>3</sub>)<sub>3</sub>;

R<sup>28</sup> is H or OH;

R<sup>29</sup> is -C<sub>1</sub>-C<sub>10</sub> alkyl, or -C<sub>1-6</sub> branched or straight chain alkyl-O-C<sub>10</sub>-C<sub>15</sub> straight chain alkyl;

20 R<sup>30</sup> and R<sup>31</sup> independently represent a phenyl radical optionally substituted with up to two C<sub>1</sub>-C<sub>4</sub> alkyl substituents;

R<sup>32</sup> and R<sup>22</sup> independently represent aryl groups substituted with at least one of C<sub>1</sub>-C<sub>12</sub> alkyl or C<sub>1</sub>-C<sub>8</sub> alkoxy group; and

R<sup>34</sup> represents C<sub>1</sub>-C<sub>8</sub> straight chain alkyl group, C<sub>4</sub>-C<sub>8</sub> branched alkyl group, or C<sub>1</sub>-C<sub>6</sub> hydroxy alkyl group.

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7. A composition of claim 6 wherein the UVA is 2-(2'-hydroxy aryl benzotriazole), 2,4-diaryl-6-(2'-hydroxy aryl)-s-triazines, or 4,6-dibenzoyl resorcinol.

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8. A composition of any preceding claim further comprising:

- (d) an additive; and
- (e) a blend stock.

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9. A composition of claim 8, wherein:

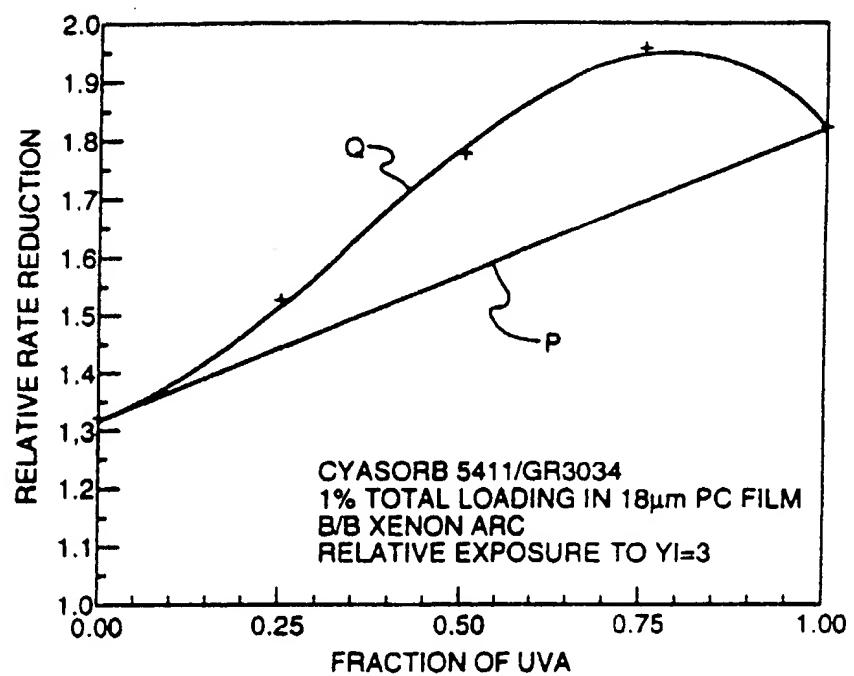
(a) the polycarbonate comprises from about 10% to about 99.9% by weight of the total composition; (b) the piperazinone and piperazine dione based HALS and the a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA taken together, comprise from about 0.05% to about 10% by weight of the total composition; (c) additives comprise from about 0.01% to about 25% by weight of the total composition; and  
40 (d) the blend stock comprises from about 0% to about 89% by weight of the total composition.

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10. A composition of Claim 9 wherein the weight ratio of the piperazinone and piperazine dione based HALS to the a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA is from about 5:95 to about 90:10.

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(11)

EP 0 900 823 A3

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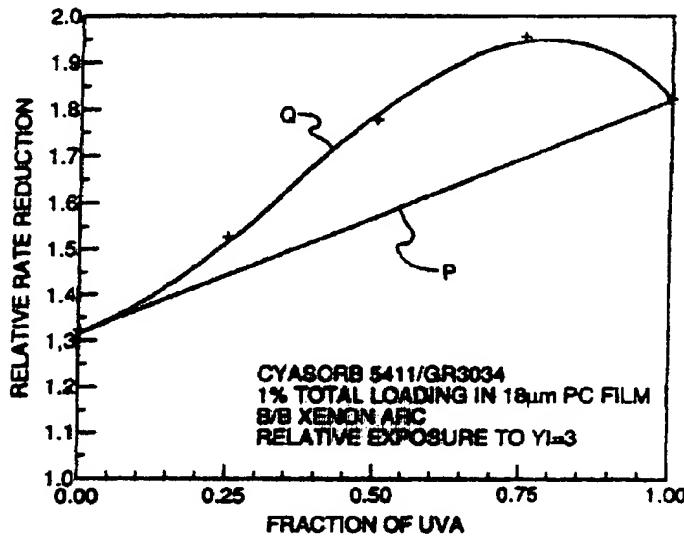
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(54) Polycarbonate compositions comprising hindered amine light stabilizers and ultraviolet light absorbers

(57) Weatherable polycarbonate compositions (formulations or blends) comprise at least one of a piperazinone and piperazine dione based HALS, and at least one of a benzotriazole, benzophenone, triazine, oxanilide, and cyanoacrylate based UVA. The combination of

these HALS and UVA exhibits a synergy that results in enhanced protection of the polycarbonate compositions by imparting photostability to the polycarbonate formulations, thereby reducing yellowing or other forms of light induced degradation.



EP 0 900 823 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 6840

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 597 854 A (BIRBAUM JEAN-LUC ET AL) 28 January 1997 (1997-01-28) * column 1, line 63 - column 20, line 13 * * column 31, line 9 - line 11 * * column 30, line 17 - line 19 * * column 29, line 62 - line 67 * * column 27, line 32 *	1-10	C08K5/3435 C08K5/3492
A	EP 0 483 488 A (AMERICAN CYANAMID CO) 6 May 1992 (1992-05-06) * the whole document *	1-10	
-----			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	18 July 2001	Lohner, P	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 6840

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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18-07-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5597854	A	28-01-1997		BR 9505169 A	21-10-1997
				CA 2162645 A	15-05-1996
				EP 0711804 A	15-05-1996
				JP 8225679 A	03-09-1996
EP 0483488	A	06-05-1992		AT 150056 T	15-03-1997
				AU 646503 B	24-02-1994
				AU 8680791 A	30-04-1992
				BR 9104627 A	09-06-1992
				CA 2054256 A	30-04-1992
				DE 69125095 D	17-04-1997
				DE 69125095 T	21-08-1997
				DK 483488 T	01-04-1997
				ES 2099721 T	01-06-1997
				GR 3022970 T	30-06-1997
				JP 3126184 B	22-01-2001
				JP 4266943 A	22-09-1992
				KR 215245 B	16-08-1999
				MX 9101498 A	05-06-1992
				NO 303393 B	06-07-1998
				US 5461151 A	24-10-1995
				US 5714530 A	03-02-1998
				US 5760228 A	02-06-1998